A superconductor to superfluid phase transition in liquid metallic hydrogen

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Although hydrogen is the simplest of atoms, it does not form the simplest of solids or liquids. Quantum effects in these phases are considerable (a consequence of the light proton mass) and they have a demonstrable and often puzzling influence on many physical properties [1], including spatial order. To date, the structure of dense hydrogen remains experimentally elusive [2]. Recent studies of the melting curve of hydrogen [3, 4] indicate that at high (but experimentally accessible) pressures, compressed hydrogen will adopt a liquid state, even at low temperatures. In reaching this phase, hydrogen is also projected to pass through an insulator-to-metal transition. This raises the possibility of new state of matter: a near ground-state liquid metal, and its ordered states in the quantum domain. Ordered quantum fluids are traditionally categorized as superconductors or superfluids; these respective systems feature dissipationless electrical currents or mass flow. Here we report an analysis based on topological arguments of the projected phase of liquid metallic hydrogen, finding that it may represent a new type of ordered quantum fluid. Specifically, we show that liquid metallic hydrogen cannot be categorized exclusively as a superconductor or superfluid. We predict that, in the presence of a magnetic field, liquid metallic hydrogen will exhibit several phase transitions to ordered states, ranging from superconductors to superfluids.

Hydrogen constitutes more than 90% of all atoms in the visible universe and contributes three quarters of its mass. It is widely accepted that hydrogen is abundant in the interiors of Saturn and Jupiter where it is both liquid and metallic [5], and the origin of their magnetospheres. The conditions in these planets, particularly those of elevated temperatures, impel a view of dense hydrogen as a classical liquid metal [6]. In what follows, a quite different view is taken for low temperatures where, for a range of densities, hydrogen is projected to take up a state which may be described as a quantum liquid metal. The notion originates both with the light mass of the proton and the form of the electronically screened, and hence density dependent, proton-proton interactions.

The proton has one fourth the mass of ^4He, which in a condensed phase at normal conditions is a classic *permanent liquid*, a consequence of high zero-point energy compared with relatively weak ordering energies arising from interactions. Similarly, zero-point energies of protons in

a dense environment are also high, and at elevated compressions there is a shift of electron density from intra-molecular regions to inter-molecular, and with it a progressive decline in the effective inter-proton attractions (both within proton pairs, and between). Because of this there is also a decline of ordering energies from interactions relative to protonic zero-point energies, and arguments have therefore been advanced [2] first to suggest the occurence of a melting point maximum in compressed hydrogen, but second that there may also be a range of densities where, as in ^4He, hydrogen may choose a fluid phase for its ground state. En route it passes through an insulator-metal transition and the phase will aptly be described as liquid metallic hydrogen, a translationally invariant two-component fermionic liquid. There is preliminary experimental evidence that a melting point maximum may indeed exist [3] and it has received recent theoretical backing [4]. Experimentally a 12.4 fold compression of hydrogen has already been achieved at around 320 GPa. Estimates suggest that LMH should appear at 13.6 fold compression at pressure in the vicinity of 400 GPa [4], whereas hydrogen alloys may exhibit metallicity at significantly lower pressures [7]. A predicted key feature of LMH at low temperature is the *coexistence of superconductivity of proton-proton and electron-electron Cooper pairs* [8]. These condensates are independently conserved, since electronic Coopers pairs cannot be converted to protonic Cooper pairs. Thus, there is no intrinsic Josephson coupling between the two condensates. This sets LMH apart from multi-component electronic condensates such as MgB_2. We therefore address some possible novel and experimentally observable physics of this new state of matter. Our goal is to discuss effects independent of pairing mechanism or other microscopic details. So in a search for *qualitatively* new physics we base our analysis solely on the *topology* of the proton-electron superconducting condensate.

The free energy appropriate for LMH will be described by the following Ginzburg-Landau (GL) model

$$F = \frac{|(\nabla + ie\mathbf{A})\Psi_e|^2}{2m_e} + \frac{|(\nabla - ie\mathbf{A})\Psi_p|^2}{2m_p}$$

$$+ V(|\Psi_{e,p}|^2) + \frac{\mathbf{B}^2}{2}; \quad \mathbf{B} = \nabla \times \mathbf{A}. \qquad (1)$$

the condensate order parameters are complex fields denoted by $\Psi_\alpha = |\Psi_\alpha|e^{i\phi_\alpha}$, where $\alpha = p, e$, with p and e referring to protonic and electronic Cooper pairs and $V(|\Psi_\alpha|^2) = b_\alpha|\Psi_\alpha|^2 + \frac{c_\alpha}{2}|\Psi_\alpha|^4 + d|\Psi_p|^2|\Psi_e|^2$. We have

introduced the masses m_e and m_p of the electronic and protonic Cooper-pairs, respectively, and $\pm e$ is the effective charge of the Cooper-pairs in the two condensates. Apart from the Josephson term $\Psi_e^*\Psi_p + h.c.$ which is forbidden, as noted above, (1) may include other terms which merely introduce small quantitative changes to the effects discussed in this paper, and which thus may be omitted. The GL free energy can be rewritten as [9, 10]

$$F = \frac{1}{2}\frac{\frac{|\Psi_e|^2}{m_e}\frac{|\Psi_p|^2}{m_p}}{\frac{|\Psi_e|^2}{m_e} + \frac{|\Psi_p|^2}{m_p}}(\nabla(\phi_e + \phi_p))^2 +$$

$$\frac{2}{\frac{|\Psi_e|^2}{m_e} + \frac{|\Psi_p|^2}{m_p}}\left\{\frac{|\Psi_e|^2}{2m_e}\nabla\phi_e - \frac{|\Psi_p|^2}{2m_p}\nabla\phi_p\right.$$

$$\left.-e\left(\frac{|\Psi_e|^2}{m_e} + \frac{|\Psi_p|^2}{m_p}\right)\mathbf{A}\right\}^2 + \frac{\mathbf{B}^2}{2}. \qquad (2)$$

The first term is recognised as the kinetic term of Gross-Pitaevskii functional for liquid ^4He, since no coupling to a vector potential $\mathbf{A}$ is present. This term may be thought of as describing an *electrically neutral* mode in the system, and is nothing but dissipationless *co-directed currents of electrons and protons carrying zero net charge*. The second term is equivalent to a gauge-invariant gradient term in an ordinary superconductor describing a charged mode in the system.

From the point of view of electronic pairing it has been suggested that at certain densities metallic hydrogen is a type-II superconductor [11, 12] i.e. magnetic flux may penetrate it in the form of vortices. When both protonic and electronic pairings occur the interesting physical question centers on whether there is a vortex structure for both, and there are several distinct possibilities. The main features of the ground state of vortex matter in this model are: (*i*) If the vortices of both components share the same core, such a composite vortex is characterized by phase windings ($\Delta\phi_e = \pm 2\pi$, $\Delta\phi_p = \mp 2\pi$), and then it has a finite energy per unit length, and carries one flux quantum [10]. Only these types of composite vortices can actually be induced by a magnetic field. By a phase winding, we mean here the line integral of a phase gradient around a closed contour. In contrast, the vortices ($\Delta\phi_e = \pm 2\pi$, $\Delta\phi_p = 0$) and ($\Delta\phi_e = 0$, $\Delta\phi_p = \pm 2\pi$) carry a fraction of flux quantum and then a logarithmically divergent energy per unit length [10]. (*ii*) In the absence of an external magnetic field, the phase transitions in (1) are driven by a proliferation of thermally excited closed loops of vortices ($\Delta\phi_e = 2\pi$, $\Delta\phi_p = 0$) and ($\Delta\phi_e = 0$, $\Delta\phi_p = 2\pi$) at critical temperatures T_c^e and T_c^p, respectively [13, 14]. We stress that in zero applied field the system is *superconducting* at *all* temperatures below T_c^e.

Next, we point out that application of an external magnetic field can change the physical state of LMH dramatically and may result in a novel type of quantum fluid.

We first consider the type-II regime. We emphasize that LMH should allow great flexibility in changing the GL parameter κ both for protons and electrons by varying the applied pressure and temperature [11, 12]. In a superconductor with only one type of Cooper pair, a lattice of Abrikosov vortices melts in a first-order phase transition at a temperature $T_M(B)$ which decreases with increasing magnetic field [13]. The physical possibilities for LMH are far richer, as we shall see. At zero temperature in an external field the system allows only composite vortices with $\phi_p = -\phi_e$ [for such a vortex the first term in (2) is zero]. However, because of thermal fluctuations, at $T \neq 0$ a vortex ($\Delta\phi_e = 2\pi, \Delta\phi_p = -2\pi$) can split *locally* into two elementary vortices ($\Delta\phi_e = 2\pi, \Delta\phi_p = 0$) + ($\Delta\phi_e = 0, \Delta\phi_p = -2\pi$) as shown in Fig. 1. Such a splitting
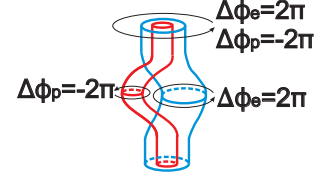

FIG. 1: Local splitting of a composite vortex line in LMH. The blue and red colors represent electronic and protonic vortices, respectively. The length scales are chosen almost equal for graphical convenience.

would result in a nontrivial contribution to the Ginzburg-Landau energy from the first term in (2), in the area in between two branches, since segments of such a loop attract each other logarithmically [10, 14]. The system (1) therefore possesses a characteristic "*vortex ionization*" temperature at which a composite flux line ($\Delta\phi_e = 2\pi, \Delta\phi_p = -2\pi$) completely splits into two elementary vortices ($\Delta\phi_e = 2\pi, \Delta\phi_p = 0$) + ($\Delta\phi_e = 0, \Delta\phi_p = -2\pi$). Such a splitting leads to a "plasma" of line vortices interacting with a logarithmic potential. This topological transition is in the $3D$ XY universality class, and should not be confused with topological phase transitions in two-dimensional superconductors. In Fig.1 the protonic and electronic vortices are represented by thin and thick lines respectively. Of the two, the protonic vortex fluctuates more because it has a *smaller* stiffness $|\Psi_p|^2/m_p$ due to *larger* mass $m_p \gg m_e$. It carries a smaller fraction of flux quantum $\Phi = \Phi_0|\Psi_p|^2/m_p[|\Psi_p|^2/m_p + |\Psi_e|^2/m_e]^{-1}$ [10] and thus has smaller energy per unit length. This leads to a "role inversion" in vortex matter: vortices in the condensate of heavier particles cost less energy per unit length than vortices of condensates of lighter particles. At low temperatures, the core size of a protonic vortex is expected to be much smaller than that of an electronic vortex because of the much larger mass of the former. However such a picture is not applicable in the immediate vicinity of critical temperature for protons, where the protonic coherence length diverges. We now proceed to discuss the LMH phase diagram at low and

high magnetic fields.

LMH in low magnetic fields. Let us first consider the low-field regime in Fig. 2, when the characteristic temperature required to split a composite vortex line, T_{SLM}, is much smaller than the melting temperature of the lattice of electronic vortices, T_M^e. Such a regime should be realizable in external fields much smaller than the upper critical magnetic field H_{c2}^e for the electronic condensate. Here, when the splitting of the field-induced composite vortex line $(\Delta\phi_e = 2\pi, \Delta\phi_p = -2\pi) \rightarrow (\Delta\phi_e = 2\pi, \Delta\phi_p = 0) + (\Delta\phi_e = 0, \Delta\phi_p = -2\pi)$ becomes of order of intervortex distances, the logarithmic interaction of the split vortices would be screened in a manner similar to that expected in an ensemble of positively and negatively charged strings. When $T < T_{SLM} \ll T_M^e$ we therefore have an Abrikosov lattice of composite vortices, which we may call a *superconducting superfluid* because of the coexistence of a neutral and charged modes, denoted **SSF** in Fig. 2. However, upon transition to the "vortex-ionized" state, $T > T_{SLM}$, we have *a lattice of electronic vortices immersed in a liquid of protonic vortex lines*. There has been *a vortex sublattice melting*, pro-

tonic superconductivity and the composite neutral mode disappear in this state, but the system remains in an *electronic superconducting state* so long as the electronic vortex lattice remains intact, i.e. for $T < T_M^e$ [13]. This phase is denoted **ESC** in Fig. 2; the phase transition separating **SSF** from **ESC**, as well as the phase **ESC** itself, have no counterparts so far in ordinary superconductors. One of the consequences of the presence of a background protonic vortex liquid is that electronic vortices carry only a fraction of the flux quantum, given by [10] $\Phi = \Phi_0|\Psi_e(T)|^2/m_e[|\Psi_e(T)|^2/m_e + |\Psi_p(T)|^2/m_p]^{-1}$, where Φ_0 is the flux quantum. This fraction will be temperature dependent and with increasing temperature should reach the value Φ_0 when $|\Psi_p| = 0$. In addition to the temperatures T_{SLM} and T_M^e, the system possesses characteristic temperatures $T_L^p(\Psi_p(B))$ and $T_L^e(\Psi_e(B))$ of thermally driven proliferation of protonic and electronic vortex loops, respectively, where $T_L^{p,e}(\Psi_{p,e}(B)) > T_{SLM}$. The zero-field limit of $T_L^{p,e}(\Psi_{p,e}(B))$ corresponds to the temperatures $T_c^{p,e}$ introduced below (2), see Fig. 2.
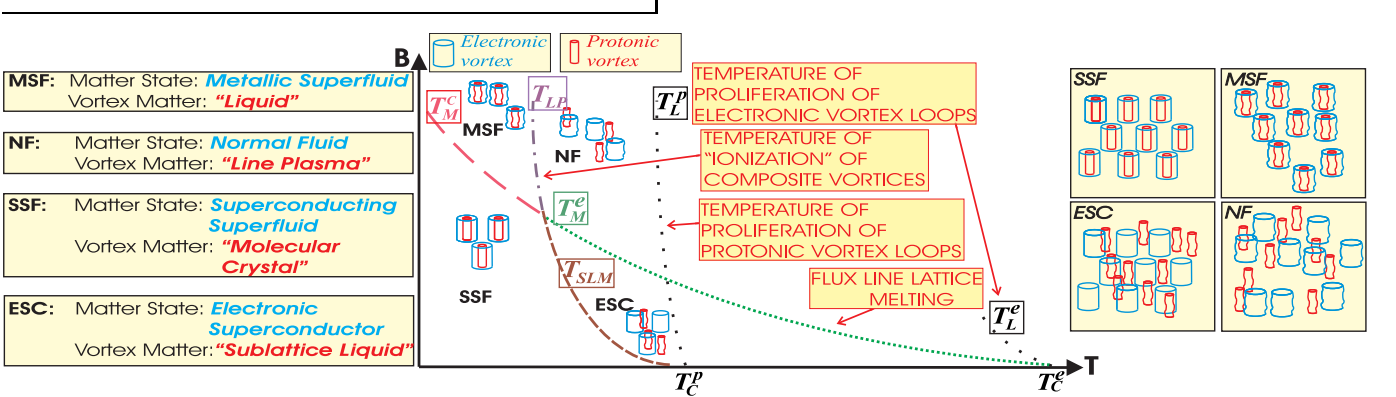

FIG. 2: A schematic phase diagram of LMH as a function of applied magnetic field **B** and temperature **T**. Phase **SSF**: Composite vortex lattice, which is a superconducting superfluid state. Phase **MSF**: Composite vortex liquid, which is a nonsuperconducting metallic superfluid state. *The transition from* **SSF** *to* **MSF** *is a superconductor-superfluid transition, and distinguishes LMH from any other known quantum fluid.* Phase **ESC**: Electronic vortex lattice immersed in a protonic vortex line liquid. This is a superconducting, but not superfluid state. Phase **NF**: Vortex *line plasma*, which emerges when composite vortex lines are fully "ionized" into an electronic as well as a protonic vortices, neither of which is arranged in a lattice. It features nonzero resistivity as well as viscosity. The low-temperature vortex-liquid phase at very low magnetic fields is not shown.

LMH in strong magnetic fields. Here the characteristic temperature required to split a composite vortex line, T_{LP}, is much larger than the melting temperature of the lattice of composite vortices, T_M^c. Such a situation occurs when (i) the bare phase-stiffness of the electronic condensate $|\Psi_e|^2/m_e$ is suppressed by the external magnetic field down to being of the same order of magnitude as the protonic stiffness, and (ii) the characteristic temperature of the melting of the lattice of composite vortices is significantly lower than protonic and electronic critical temperatures (e.g. the electronic GL parameter

κ should be large, which should be achievable through choice of density [11, 12]). The phase diagram then features the following hierarchy of characteristic temperatures: (i) T_M^c - the melting temperature of the lattice of composite vortices, (ii) $T_{LP} > T_M^c$ - the "vortex liquid" to "vortex plasma" transition temperature associated with fluxline splitting $(\Delta\phi_e = 2\pi, \Delta\phi_p = -2\pi) \rightarrow (\Delta\phi_e = 2\pi, \Delta\phi_p = 0) + (\Delta\phi_e = 0, \Delta\phi_p = -2\pi)$. As noted, this transition has a $3D$ XY universality class. We emphasise that this transition is very different from the sublattice melting transition considered above.

Next, we examine the physical consequences of this hierarchy of characteristic temperatures. At low temperatures, the magnetic properties are controlled solely by the charged mode, which is described by the second term in (2). That is, at magnetic fields below the $T_M^c(B)$ line, the system exhibits a phase which is a field-induced *lattice* of composite vortices ($\Delta\phi_e = 2\pi, \Delta\phi_p = -2\pi$) for which $\phi_p = -\phi_e$ and the first term in (2) is exactly zero. This corresponds to the *superconducting superfluid* discussed above. However, increasing the magnetic field to cross the $T_M^c(B)$ line now leads to a first order melting transition from a lattice to a liquid of composite vortices. This transition is completely decoupled from the neutral superfluid mode, while superconductivity is destroyed. *It is therefore a first order phase transition from a superconductor to a superfluid.* This distinguishes LMH from any other known quantum fluid. It naturally requires a revision of current classification schemes of quantum fluids into the two categories of superconductors and superfluids. Indeed, the metallic superfluid state, denoted **MSF** in Fig. 2, acquires all the attributes of superfluidity of neutral atoms like ^4He even though microscopically it originates in a liquid of *charged* Cooper pairs.

We note that **SSF** phase is characterized by off-diagonal long-range order (ODLRO) in both fields $\lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} < \Psi_\alpha(\mathbf{r})\Psi_\alpha^+(\mathbf{r}') >\neq 0$ for $\alpha = p, e$. In the **MSF** state, the phases of both fields are disordered and there is no ODLRO for superconducting order parameters ($\lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} < \Psi_\alpha(\mathbf{r})\Psi_\alpha^+(\mathbf{r}') >= 0$). In contrast, the *neutral mode* retains ODLRO, manifested by the preserved order in the phase sum ($\phi_p+\phi_e$). From this follows a counterpart to the Onsager-Penrose criterion [15] *for metallic superfluidity:* $\lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} < \Psi_p(\mathbf{r})\Psi_e^+(\mathbf{r}') >\neq 0$. Under such circumstances, the system is incapable of sustaining a dissipationless charge current, yet is capable of sustaining dissipationless massflow and consequently a vortex lattice induced by *rotation* as is possible in superfluid ^4He. A rotation of a high-pressure diamond cell with hydrogen can be performed in an experiment in the presence of a cooling system, making such a rotating superfluid state experimentally accessible in principle. An even more intriguing possibility appears in case a rotation of liquid metallic deuterium since the deuteron has also spin degrees of freedom. Increasing the temperature further produces an "ionization" of composite vortices. Eventually superfluidity also disappears and we are left with a metallic normal fluid; this corresponds to the phase denoted by **NF** in Fig. 2.

These observations should be of importance in experimentally establishing that hydrogen may indeed take up a low temperature liquid metallic state. Experimental probes of the states of systems confined to high presure diamond cells are limited, but nonetheless application of external fields as well as the use of induction coils have already been successfully used to detect superconductivity at high pressures. The latter technique should also permit flux noise experiments.

Our main points may be summarized as follows. (*i*) The vortex matter in LMH is principally different from vortex matter in ordinary metallic superconductors. Our analysis shows that starting from a system of two types of fermions which form two distinct types of Cooper pairs, we arrive at what can be viewed as a "dual condensed matter of vortices". The vortices can be mapped onto a system of two types of charged strings which may be viewed as "extended line particles" with "*reversed*" roles, namely the electronic vortices playing the role of "heavy particles" and protonic vortices being "light particles". Then, the Abrikosov lattice of composite vortices may be interpreted as a molecular crystalline state, which, at strong external fields undergoes at T_M^c a transition into a "molecular liquid" and at higher temperature to a "plasma" state. In contrast, at weak external fields we find a "sublattice melting" transition, an intermediate state of *vortex* matter which has a counterpart in classical condensed matter physics as e.g. atomic sublattice melting in AgI. (*ii*) A particularly intriguing circumstance is that our analysis shows that an experimental realization of LMH would mean that we have at hand a genuinely novel system which exhibits *a phase transition from a superconductor to a superfluid, or vice versa, driven by a magnetic field.* This counterintuitive fact may require a revision of the standard classification scheme of quantum liquids into superconductors and superfluids.

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